DEVELOPMENT OF WATER-BASED FRACTURING FLUIDS

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By

Clay Bonin
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Approved by

Dr. David Cole

School of Earth Sciences

TABLE OF CONTENTS

ABSTRACT

The physical and chemical properties of unconventional gas shale reservoirs differ significantly from those of conventional reservoirs requiring stimulation of the formation to improve economic recovery rates. Marked improvement in our understanding of the heterogeneous complexities of gas shale formations, new drilling methods and targeted design of novel frac fluids have all converged to make extraction of gas tight formations economically viable. New methods in well stimulation in which the rock is fractured by a pressurized frac fluid now allows the U.S. to expand its domestic production of hydrocarbons to a point where we are now more self-reliant on our own subsurface resources. The technological advances have led to a significant change in the global energy landscape.

This study focused on the nature of the frac fluids used to stimulate gas production. We first provide a brief overview of the hydraulic fracturing that includes a discussion of slickwater frac fluid design and a historical perspective on the evolution of frac fluids. The geological characteristics and pore features of the highly productive Marcellus gas shale are used as a basis for method development that targeted the FracFocus.org web site. This expansive data base provides detailed accounting of the chemical additives used in hydraulic fracturing. Data analytic assessment of chemical data reported for the Marcellus Formation resulted in a unique compilation of specific chemical additives that industry uses to optimize gas recovery. The composition of the Marcellus frac fluid blend indicates how the industry tailors the chemical additives to take advantage of key formation characteristics including subsurface temperature, pressure, pore type and organic matter type.

ACKNOWLEDGEMENTS

Thank you to my wife, mother, sister and family for everything. I am in a debt to you all in which I can never repay. Thank you to Dr. David Cole, Dr. Julie Sheets and all SEMCAL members. Thank you to the School of Earth Sciences at The Ohio State University for affording me the opportunity at an education. Thank you to the company who gave me my first job in oil and gas, and to the many others that followed. This is for my Grandfather, Solomon.

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

Hydraulic fracturing is currently the primary stimulation method for hydrocarbon production in unconventional gas and oil reservoirs with characteristically low and restrictive permeability. Fracturing is used with the intent to create a synthetically enhanced permeability surrounding the borehole, particularly in the lateral wellbore zones; however, the overall effective permeability of a formation outside the enhanced permeability remains unchanged by this process. Figure 1 shows a schematic horizontal well in the subsurface taken from the Schlumberger web site. In the last decade and a half, the percentage horizontal and directional drilled wells have increased exponentially, and along with this trend, we have observed a marked change in the nature of the types of fluids used to pressurize the formation.

When fracturing a horizontal wellbore, the design of the frac fluid is an essential aspect of the production process required to ensure: (a) an optimal fracture width to allow proppant entry into the fracture (synthetic or intrinsic), (b) an adequate transporting matrix for the proppant from the top side down to the ends of the intended fracture zone, (c) generation of an engineered pressure to properly mitigate the growth (in all fracture planes) and (d) manageable control over fluid loss. The frac fluid should be designed to yield the desired viscosity which must not be detrimental to the natural fracture conductivity or the inherent reservoir permeability (formation damaging), inexpensive and able to lessen fluid loss.

These requirements have been standard since the beginnings of hydraulic fracturing. However, to better understand modern day fracturing fluids, it is important to examine the evolution of fluid composition and the application of stimulation methods. Hydraulic fracturing is not new but the chemistry and development of water-based fluids is still young and evolving rapidly. The objective of this study is to examine the history and evolution of frac fluids, the types of frac fluids deployed, the physical and chemical requirements of a good fracturing fluid and their limitations, and an example of how additives interact with the formation.

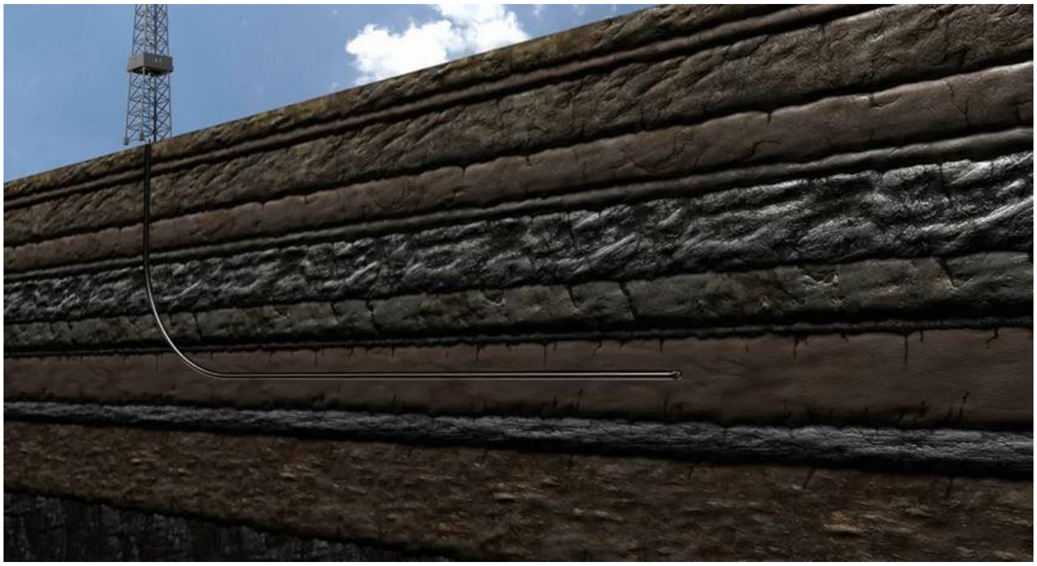

Figure 1: Schematic cross section view of a horizontal well. (Schlumberger, 2018)

A Note on the Importance of Pressure

In the treatment of hydraulic fracturing, it is critical that the wellbore be perpendicular to the minimal stress (S_{min}) fields in the targeted formation. Ideally, the fractures will form approximately perpendicular to the axis of S_{min} (Yew, 1997). Concerning deeper reservoirs (< 10,000 feet), the S_{min} stresses are again perpendicular to the lateral wellbore and vertical fractures will occur if properly stimulated. The minimum and maximum stresses (actual), and stress field orientation, are determined first by balancing the vertical geostatic (overlying lithostatic column) stress and the horizontal stress by the theory of elasticity. More specifically, the geostatic values must be adjusted for in a porous formation that is filled with a fluid by giving a corrected poroelastic value and a hydrostatic pressure (Yew, 1997). The horizontal value can be derived using a corrected vertical value along with the Poisson ratio.

Knowledge of the stress values and stress orientations of a formation is vital to calculate the pressure burden (upper limit) at which the opening of a fracture will begin. The pressure limit is then used during the engineering and design of the stimulation schedule. A treating pressure can then be implemented that will not damage the formation but still be conducive to fracture propagation and ultimately proppant (typically silica sand) placement. The upper bound of this pressure can be estimated using a formula given by (Von Terzaghi, 1923):

$$P_b = \ 3_{Smin} -_{Smax} + T - p$$

Where, P_b is fracture pressure, 3_{Smin} is minimal horizontal stress, $Smax$ is maximum horizontal stress, T is tensile strength of rock material and p is pore pressure. Figure 2 shows an example of the trends of pressure (in psi/ft.) on the Marcellus. The over pressure area lies almost entirely within the state lines of Pennsylvania. This pressure regime influences the frac fluids used in this area. The nature of Marcellus frac fluids are described in a later section.

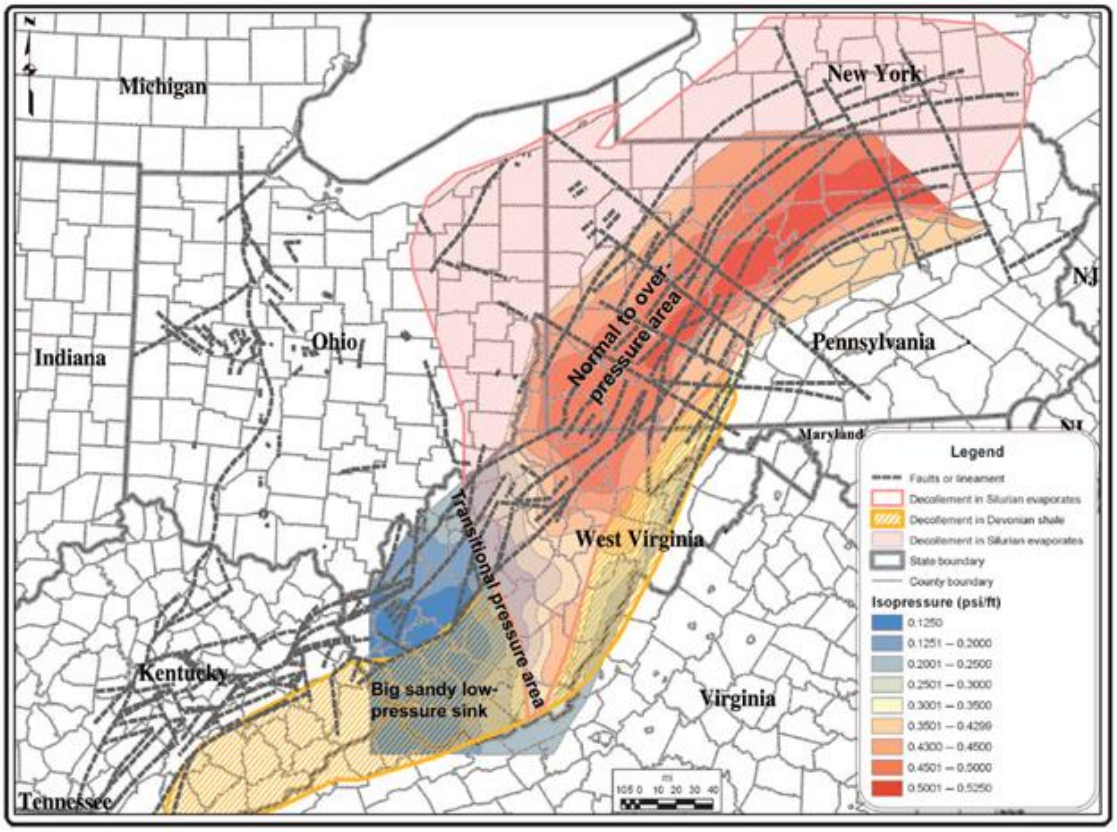

Figure 2: Relationship of Marcellus Shale pressure trends (Zagorski et al., 2012).

It is imperative that faults be known in a formation before drilling. Knowledge of stress field orientations (in-situ) plays a vital role. If a horizontal wellbore intercepts a fault plane then there is a chance of unintentional frac fluid loss which will likely lead to a financial and environmental catastrophe. Precise understanding of the stresses is established with the help of seismic methods pre-drilling, and further refined with coring samples, well logs and microseismic mapping conducted during the first wellbore drilled into a prospective zone. All subsurface operations come with inherent risk but sound planning coupled with successful execution mitigates potential risk.

FRAC FLUID APPLICATION

In hydraulic fracturing, a treatment schedule is the finalized plan for the stimulation of a reservoir via hydraulic fracturing along a horizontal wellbore. By the time a wellbore fracturing is scheduled, several steps have been completed in the overall process from the spud date to the production of hydrocarbons on the top side ready to be transported for refinement. Schedules can vary greatly in execution and most of them break down a wellbore into multiple sections called stages. Each stage (formation section) may be treated differently based on pressure over burden (see Fig. 2 as an example of the Marcellus), lithology, fluid saturation and TOC (total organic content). Figures 3 and Figure 4 are examples of well pads using several horizontal wells as schematically shown in Figure 1.

Figure 3. The pictured well pad showing the fracturing treatment of a single well in the Woodford shale play in central Oklahoma. Alta-Mesa Energy completion. (Clay Bonin, 2015)

Figure 4. A well pad showing the fracturing treatment of multiple wells in the Marcellus shale play in West Virginia. AEP completion. (Clay Bonin, 2014)

The pumping of a frac stage can last from fifteen minutes to over four hours in extreme cases, contingent upon the design and intent of the schedule. During the high pressure pumping operation (when frac fluid is forced into fractures) is the only period during which most wellbores will undergo pressures that will force reverse fluid flow (back into the formation). The vertical growth of fractures can measure up to a few hundred feet above the pay zone (i.e., area of formation containing mature recoverable hydrocarbons), but in reality, the fracture propagation, as shown in Figure 5, will be limited by a natural rock barrier above and below the pay zone. Another factor limiting fracture propagation is the cumulative loss of frac fluid (fluid leak off) as it disperses into the formation. This cumulative loss is due to increasing surface area in contact with the frac fluid.

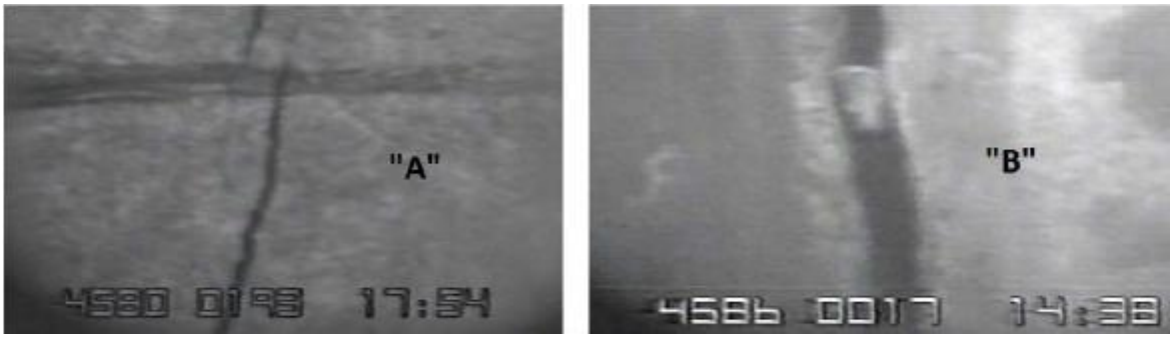

Figure 5. Borehole images in an open-hole completion. "A" displays narrow fractures stopping and starting, interrupted by a shale. "B" is a well-developed fracture in limestone. (Schlumberger, 2018)

Propagating a fracture up through thousands of feet of rock is not possible, due to the limits levied by naturally occurring rock barriers, frac fluid leak off and the natural occurring stress fields, which may be different than the targeted formation or pay zone. The intent of hydraulically fracturing shale formations is to create a flow path for hydrocarbons from isolated sections of the reservoir to the wellbore via induced effective permeability. In addition to newly created fractures these paths can be established through the widening of existing micro-fissures, micro-fractures and other frail zones inside the shale forming a secondary high permeability path in the existing shale formation matrix.

Slickwater Frac Fluid Design

Frac fluids can be divided into water-based, oil-based, alcohol-based, emulsion, or foam-based fluids. The addition of polymer hydration chemicals, crosslinking chemicals, and temperature related degradation are all processes that frac fluid compositions experience. Modern enhancements have focused largely on improving frac fluids rheological performance and temperature stability. A number of frac fluids performance criteria must be met requirements instantaneously. Fluids need be stable at high temperatures (200 to 400 Fahrenheit), pumping rates (measured in barrels per minute BPM), and variable shear rates (Economides and Nolte, 2009).

These elevated subsurface conditions can cause frac fluids to degrade resulting in a reduction in viscosity thus causing a premature settling out of the proppant (typically silica sand) before the treatment schedule is completed (Economides and Nolte, 2009). Most frac fluids are aqueous liquids that have been gelled (hydration polymers). Typically, the frac fluids are gelled by a polymeric additive. The now thickened fluid has increased viscosity that aids in keeping the proppant particles within the frac fluid during the scheduled operation until they are dispersed throughout the area of synthetic permeability.

Water-based frac fluids, also known as slickwater fluids, in which the dominant agent is polymeric are not so damaging to a formation compared to heavier fluids with higher viscosity and specific gravity (Table 1). Slickwater fluids are generally used for more precise targeting of the intended synthetic permeability zone, whereas heavier fluids (linear and crosslinked gels) may lead to the unintended migration of this zone and the possible communication between to wells in close proximity (Economides and Nolte, 2009). Slickwater technology and methodology, pioneered in the 1980s, are not as expensive as linear gel treatments. The technology allows for conditions where fluid and proppant volumes can be reduced, and treatment schedules (pump time) can be reduced significantly, lowering the costs related to equipment and personnel, and satisfying environmental concerns. Unlike slickwater, conventional linear gel treatments tend to leave substantial amounts of formation residue and require additional chemicals (breakers) to dissolve the gel once inside the formation.

Table 1: Typical additives in slickwater frac fluids in shales (from FracFocus.org)			
Most common slick water frac additives	Composition	CAS #	% of shale treatments that use this additive.
Friction Reducer	Polyacrylamide	9003-05-8	Nearing 100%
Biocide	Glutaraldehyde	111-30-8	80%
Scale Inhibitor	Phosphonate and polymers	6419-19-8	15-25%
Surfactant	Numerous	Numerous	20-25%

In comparison to slickwater to conventional linear gel, slickwater frac fluids can generate comparable or better production results (Shah and Kamel, 2010). Slickwater fracturing has been increasingly applied in the stimulation of unconventional shale gas reservoirs (Cheng, 2012). Compared to crosslinked gel-bearing fluid (a chemical additive, typically borate, used to link the linear gel into a higher viscosity gel), slickwater frac fluid has key advantages, including a higher probability of creating more complex fracture networks, inflicting less overall formation damage and allowing ease of cleanup since no breaker additive is needed nor substantial formation residues.

The Evolution of Frac Fluids

Hydraulic fracturing treatments are not new in the oil and gas industry. The first reservoir fracturing experiment was conducted in 1947, and the process in was adopted more widely on a commercial basis around 1950. The very first horizontal well drilling took place in the 1930's and was commonplace by the late 1970s. Literally millions of fracturing treatments have been conducted and tens of thousands of horizontal wells completed over the past half century. Shale gas such as from Devonian Period shales including the Marcellus, are not new hydrocarbon generating sources. These shales serve as sources for the shallower wells of eastern Pennsylvania.

A fracturing fluid requires sufficient viscosity (50–1,000 cP) to open the fracture (0.5–2.5 cm) and to transport proppant from the topside down the well casing and in to the fractures (Veatch, 1983) under an applied pressure (treating pressure) determined beforehand. Treating pressures range from 4,000psi up to 14,000psi. Various additives are mixed in collaboration one another to create specific treatment fluid types. These treatments, borehole directions, proppant sizes, treatment fluids and additive types can be roughly classified into three distinct time periods from 1947 through 2010 (Gallegos and Varela, 2015).

In the first period from 1947 to 1952, the frac fluids were oil-based, composed of crude oil, and often gasoline, congealed with napalm (Gulbis and Hodge, 2000). Of those frac fluids reported, the majority were characterized as water, oil, acid (commonly HCl or HBr) and explosives. A shift in technology during this time moved away from fracturing with explosives and acid etching (matrix acidizing) to fracturing by means of the injection of oil-based fluids with sand to hold open the fractures, a process developed initially for stimulating sandstone formations (Elbel and Britt, 2000). These treatment methods were applied primarily to vertical wells for oil production stimulation.

The following era spanning 1953–1999 witnessed a significant development in the introduction of water as a base in fracturing fluid formation, more specifically in 1953 (Montgomery and Smith, 2010). Shortly thereafter, use of water-based fluids including proprietary formulations from field service-company increased in use. The beneficial reasons for water use quickly manifested with their expanded use. The near incompressibility of water allowed for efficient transfer of pressure from the pumps on the topside to the formation at the bottom of the wellbore. Other characteristics of water that make it appealing for use are its use in treatment include its neutral pH, thereby avoiding degradation effects produced by an acidic or basic medium, and that it is a universal solvent. Other logistical advantages are the water's availability and relative low cost. Soon the recorded numbers of proppant use began to rise (silica sand namely) around 1953. Sand is regarded as the most common proppant mostly because of its obvious logistical advantages. The increases in the use of silica sand is supported by open source records (IHS Energy, 2011).

Less than 1% of the records in accessible datasets document the use of ceramic proppant, resin-coated ceramic proppant, and resin-coated silica sand (Beckwith, 2010). During 1953-1999, over 990,000 treatments were applied in vertical oil and gas wells (IHS Energy, 2011). The use of water-based frac fluids is concurrent with the evolution and adoption of numerous different additives (due to neutral pH and solvency). Each additive was designed to enhance fracturing treatments, as dictated by formation attributes.

Following the development of water as the base treatment fluid, gelling additives like guar gum and cellulose byproducts were used to increase fluid viscosity. These gel-bearing frac fluids were crosslinked using potassium pyroantimonate when >7 pH, borate at when <7 pH, or even aluminum to increase the weight of water-soluble polymers (Ely, 1985). This crosslinking allowed the frac fluid to more transport proppants effectively at low temperatures.

As wellbores reached further depths engineers were faced with newer problems of elevated temperatures coupled with higher pressures. Temperature reactive gelling additives were developed out of necessity. The HEC polymer-based gels and secondary gels treated with glyoxal, which would then activate under the elevated temperature encountered once the fluid reached the formation (Ely, 1985). These resilient higher temperature gels were crosslinked using zirconium(IV) and titanium(IV) to create crosslinked guar gel frac fluids instead of borate (Ely, 1985) which had a poor temperature stability by comparison. During this era, 20/40 silica sand (425–850 μm) was used in 70% of the frac treatments (IHS Energy, 2011) and was the foremost silica particle size throughout 1990s and 2000s (Beckwith, 2010).

The evolution of frac fluid design and application underwent more change in the most recent period, 2000-2010. During this period of time fracturing treatment fluids and additives totaled nearly 750,000 (IHS Energy, 2011). From 2007 to 2009, rapid expansion of shale gas production began in states outside of Texas. The extraordinary increase in fracturing treatments around 2008 coincides with extensive use of advanced slickwater frac fluids. Slickwater is mostly water (99% or greater) with other additives in variable quantities that increase fluid velocity and proppant transport through the wellbore and into the formation at a targeted depth.

Silica-based proppant smaller than 20/40 size emerged in combination with slickwater treatments of unconventional hydrocarbon reservoirs. The size of the silica is very important. Typical silica sand sizes are generally between 8 and 140 mesh (106 μm - 2.36 mm). Examples include: 16-30 mesh (600 μm – 1180 μm), 20-40 mesh (420 μm - 840 μm), 30-50 mesh (300 μm

– 600 μm), 40-70 mesh (212 μm - 420 μm) or 70-140 mesh (106 μm - 212 μm). The rise in slickwater fluids coincided with the nearly 60,000 directional or horizontal wellbores drilled between 2000-2010 (Gallegos and Varela, 2015). The majority of wellbores were drilled vertically; however, the percentage of horizontal/directional drilled wellbores went from 6% of in 2000 to 42% in 2010. Approximately 75% of horizontal/directional wellbore treatments completed in this period were intended to produce natural gas and the remainder to produce oil resources (Gallegos and Varela, 2015).

GEOLOGIC CONDITIONS

Black Shales

Black shale is a dark mudrock containing organic matter and clay to silt sized mineral grains that accumulated together. Most shales contain 1% or more organic carbon; 2-10% is a common range. A few shales contain more than 20% organic carbon (Swanson, 1966). Stepped-heating pyrolysis experiments yield variable amounts of liquid and gaseous hydrocarbons with the amount depending, in part, on the nature of the original organic material as well as the subsequent burial history. Below we describe the Marcellus Formation which is the focus of our frac fluid chemistry assessment.

Middle Devonian Marcellus Formation

An understanding of unconventional reservoir geology is becoming better established. This understanding encompasses the depositional (stratigraphy) and maturation histories of these reservoirs. Gas shale plays contain a range of hydrocarbon types, and in some cases, shales exhibit very tight gradations from volatile oil to retrograde gas condensates. Hydrocarbon type can change across the gas shale play over distances as small as a few miles or less depending on the prevailing geologic features.

In addition to variability over macro-distances, a key challenge facing the industry is understanding the small scale petrophysical features of unconventional shale (Economides and Nolte, 2009). Efforts to characterize the pore space in these unconventional shale plays are focused on the micrometer to nanometer scale imaging to better understand the pore network within the host mineralogy and its textures, and associated kerogen components. Figures 6-8 presents a series of SEM images as examples of these features.

The morphology of the pore space in the rock has an impact on the thermodynamic phase behavior of the hydrocarbon fluids, specifically for the liquids dominant (volatile oil or retrograde condensate fluid) hydrocarbon systems. Hydrocarbon fluids confined to very small pore volumes (10s of nm^3) exhibit different structural, dynamical and reactive properties compare to bulk fluids depending on the dimensions of the pore confinement (Cole et al. ,2013; Striolo and Cole, 2017). This is contrary to traditional reservoirs where hydrocarbon properties are controlled primarily by coarse-scale physical pore structures in addition to pressure, and temperature. The SEM images shown below confirm the potential for hydrocarbons resides in the small pore volumes formed in the evolved organic matter.

The Marcellus Formation is a unit of the Middle Devonian Hamilton Group. Marcellus is classified as a distal marine mudstone deposited within in the Appalachian Basin. The time of deposition occurred during the Acadian orogeny (Ettensohn, 1985). The maximum burial in the western Marcellus was 3.5 km and maximum temperature was 120°C (calculated using vitrinite reflectance method). In the east, the maximum burial and temperature was 6 km and 150°C, respectively (Beaumont et al., 1987). The pressure regimes can be calculated at any given point using the formation isopressure values provided in Figure 2.

Pores are at the center of interest in the Marcellus. There are different types of pores and pore geometry, but of these, the most important are the organic-matter-hosted pores. (Milliken et al., 2013) have characterized organic matter pores into four main types based on distribution, complexity and geometry (Fig. 6).

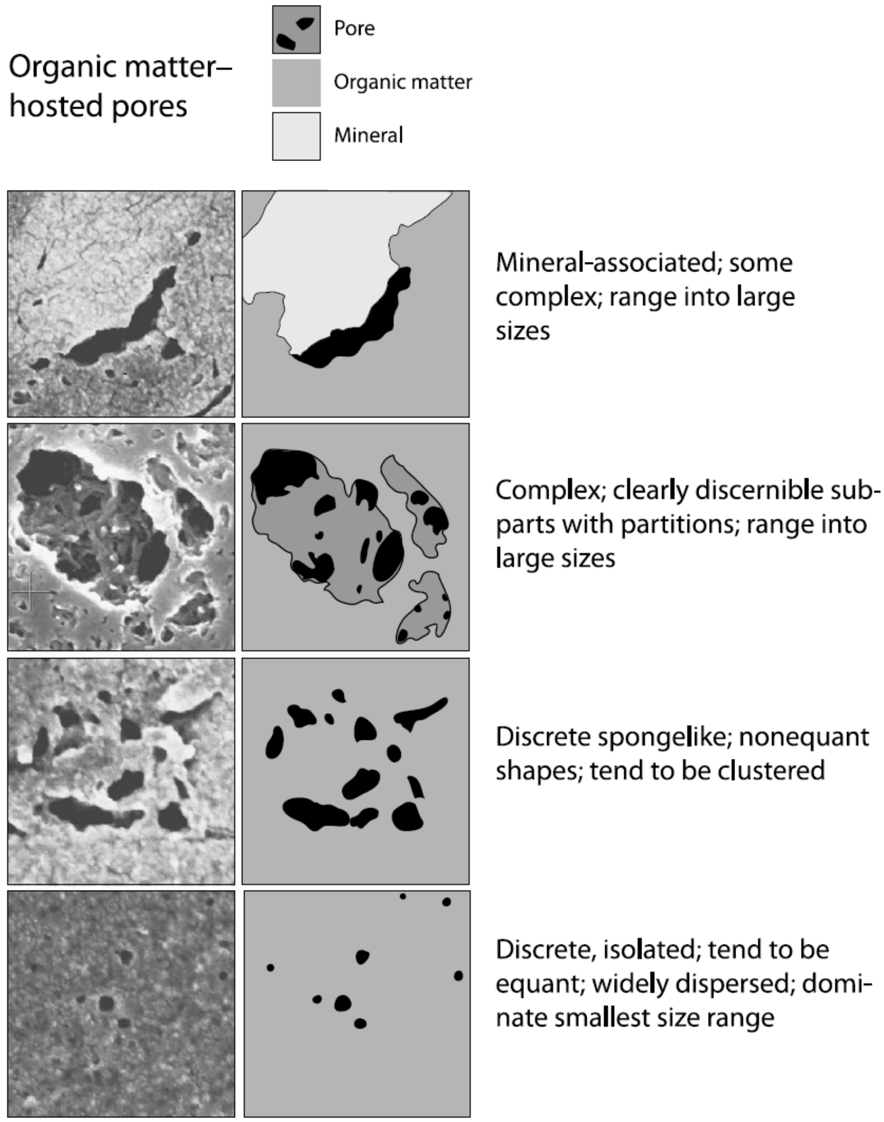

Figure 6: Qualitative classification of OM-hosted pores, illustrated from secondary electron images (left) with interpreted line drawings (right). (Milliken et al., 2013)

Diverse pore types are observed in the Marcellus, including both mineral-surrounded pores and organic matter-hosted pores. The following Figure 7 and Figure 8 show images from the lower thermally mature west region of the Marcellus followed by images of the higher thermally mature east region, respectively.

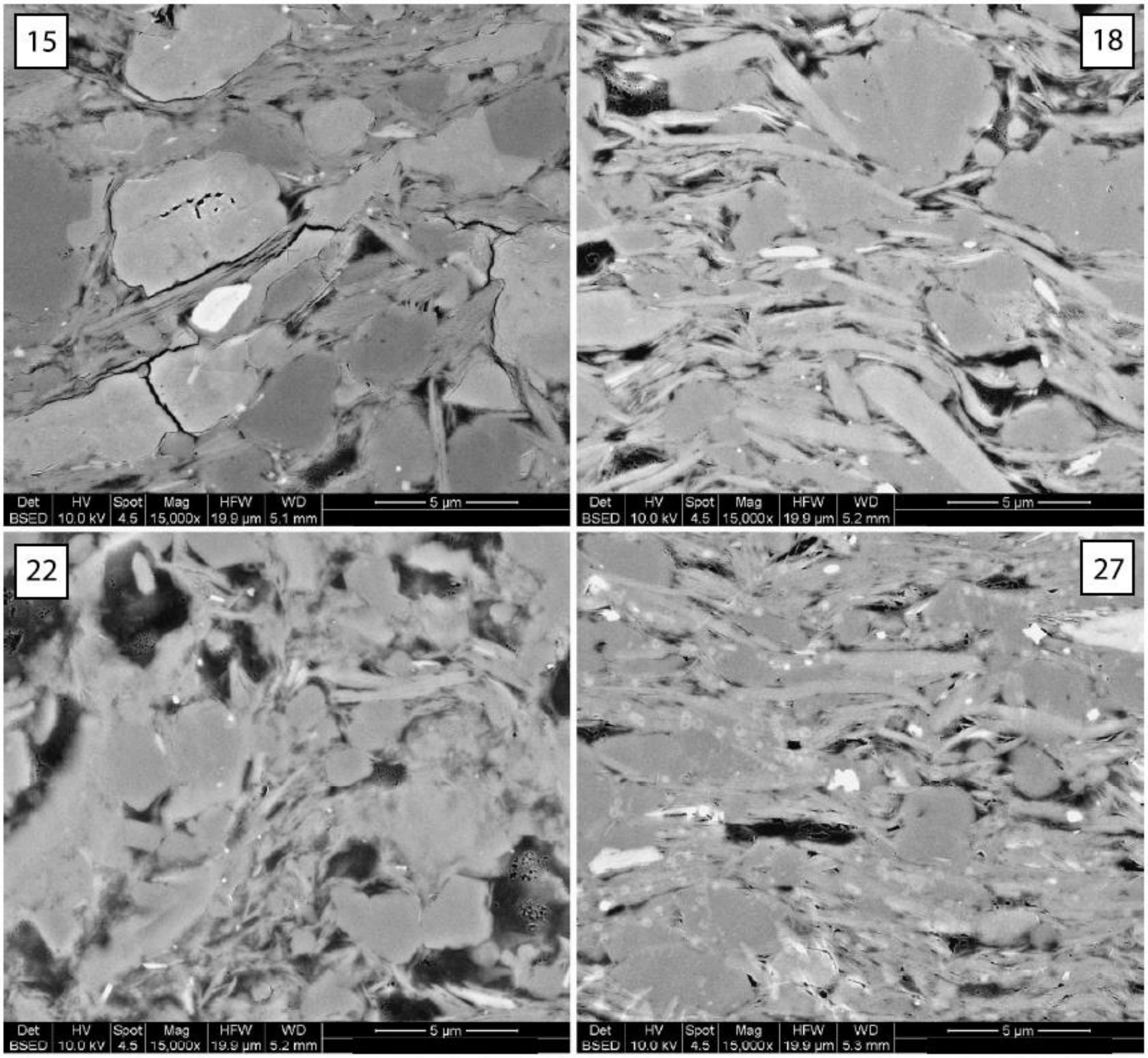

Figure 7: Backscattered electron SEM images of east Marcellus, images dominated by siliciclastic grains of quartz and feldspar and micas. Darkest regions are organic matter, whitest are pyrite (Milliken et al., 2013)

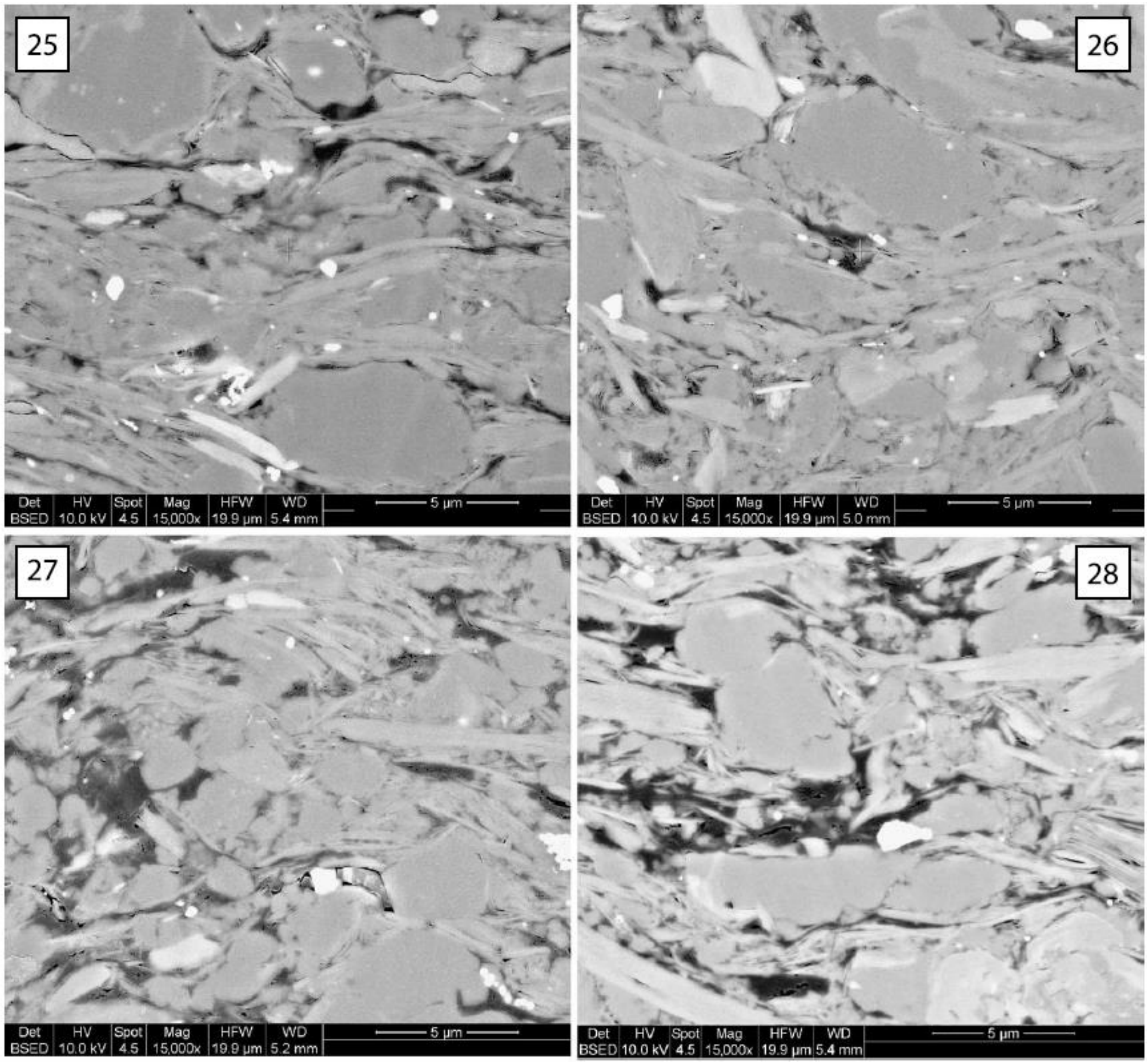

Figure 8: Backscattered electron SEM images of west Marcellus, images dominated by siliciclastic grains of quartz and feldspar and micas. Darkest regions are organic matter, whitest are pyrite. (Milliken et al., 2013)

Generally, the Marcellus images presented here represent good examples of pore systems that largely controlled by the evolution of organic matter (Milliken et al., 2013). The sub-micron scale Marcellus pores that likely host the gas are difficult to characterize, especially in 3-dimansion thus demonstrating the interplay between porosity (storage) and effective permeability (interconnectivity of storage) very challenging. Engineering and optimizing the connection between this pore space to top side production is the industry challenge, and commercially viable production cannot be realized in such shales without creating a secondary (synthetic permeability) hydrocarbon pathway achieved during hydraulic fracturing. Even with successful fracturing treatments, economic production is not guaranteed as many variable influence the outcome, not least of which is how the pores hosting gas respond to the presence of the frac fluid.

METHODS

Data Mining

During the late 2000s, the public interest in understanding the chemical compositions of frac fluids peaked. In response, the GWPC (Ground Water Protection Council) and the IOGCC (Interstate Oil and Gas Compact Commission) began a national frac fluid chemical registry, FracFocus.org. Energy operators began to comply and voluntarily uploaded disclosures on their frac fluids used in treatments. Disclosures included information about the stimulation treatment (energy operator name, unique well identification, wellbore location, total water volume) and frac fluid composition (base fluids, polymers, additives).

GWPC provides an archive of roughly 39 thousand disclosure submitted to FracFocus.org prior to March 1, 2013. Each record provides trade names of additives, additive purpose, and the maximum concentration of each additive in the overall frac fluid. An example disclosure with artificial input is given in Figure 9.

Data Extraction, Normalization and Standardization

To facilitate retrieval of data (39,136 PDF files), the disclosures were changed to Extensible Markup Language (Microsoft Excel XML) files. The XML data was then converted to comma-separated values (CSV) files. CSV data was then loaded into a database program (Microsoft Access 2013) and more than 98% (38,530 of 39,136) of the disclosures were included in the database for indexing and use. Data records were scrubbed that contained duplicate API well numbers (unique to a well), and then records that did not fall in to the time frame of the fracture date between January 1, 2011, and February 28, 2013.

Compiling the data into a single database for use in analysis and interpretation proved to be difficult and time consuming. The data made available to the public domain from FracFocus.org are cumbersome, incomplete and inconsistently formatted. After numerous attempts at data aggregation into a single data set it became apparent that quality control of submitted disclosures from energy producers was not a priority. During a recent industry internship for a stimulation group part of my responsibilities included the completion and submission of such disclosures. The template used was, and still is, a less than impressive excel spreadsheet. A disclosure record could be rendered effectively useless during data mining due to a single keystroke error while entering information into the spreadsheet.

Hydraulic Fracturing Fluid Product Component Information Disclosure

Fracture Date:	1/10/2011
State:	Texas
County:	Greer
API Number:	99-123-45678
Operator Name:	Company ABC
Well Name and Number:	Well XYZ
Longitude:	-94.611274
Latitude:	27.035098
Long/Lat Projection:	NAD27
Production Type	Oil
True Vertical Depth (TVD):	14,637
Total Water Volume (gal):	3,107,561

Hydraulic Fracturing Fluid Composition:

Trade Name	Supplier	Purpose	Ingredients	Chemical Abstract Service Number (CAS #)	Maximum Ingredient Concentration in Additive (by mass)**	Maximum Ingredient Concentration in HF Fluid (by mass)**	Comments
Water	Company A	Carrier/Base Fluid	Water	7732-18-5	100.00	84.09743	
Sand		Proppant	Crystalline Silica	14808-60-7	100.00	12.32189	
Hydrochloric Acid	Company B	Acid	Hydrogen Chloride	7647-01-0	40.00	1.09518	
Aceticplex 50	Company B	Petrochemical industry: Oil Well Acidizing, Iron Sequesterant	Acetic Acid	64-19-7	50.00	0.01187	
Plexgel 907L-EB	Company C	Viscosifier for water	Distillate, petroleum, hydrotreated light	64742-47-8	60.00	0.21713	
			Propylene Pentamer	15220-87-8	60.00	0.21713	
			C-11 to C-14 n-alkanes, mixed	Mixture	60.00	0.21713	
Plexaid 430	Company A	Gel stabilizer	Sodium Thiosulfate	7772-98-7	30.00	0.02214	
Buffer 12	Company D	pH buffer	Potassium Hydroxide	1310-58-3	23.00	0.04030	
Plexgel Breaker HT	Company B	Encapsulated Oxidizing gel breaker	Ammonium Persulfate	7727-54-0	90.00	0.00144	
Plexcide 24L	Company B	Biocide	Tetrahydro-3, 5-Dimethyl-2H-1,3, 5-Thiadiazine-2-Thione	533-74-4	24.00	0.01131	
			Sodium Hydroxide	1310-73-2	4.00	0.00189	
Greenhib 677	Company C	Oilfield Scale Inhibitor	Salt of Phosphono-methylated Diamine	NA	25.00	0.01172	

Figure 9: An example of an individual FracFocus.org disclosure record with fictional data used for illustration purposes only (from FracFocus.org).

In its original intent FracFocus.org was created to meet local informational needs of the general public, but the massive number of records found in the registry allows for insights into the composition of frac fluids used in specific basins and shale formations.

RESULTS

Interest in the productive Marcellus shale stems from my past work experience of drilling and treating hundreds of wells in the play. Therefore, I narrowed down the data analytics on frac applications to Marcellus shale wellbores treated within the state of Pennsylvania

In Table 2, the most commonly used additives in the Marcellus Formation are compiled and listed in descending order of highest to lowest frequency of reporting in the industry chemical disclosures. A number of these entries are of more specific to Marcellus shales whereas others more generally used in many for top side engineering applications were not included. As such, this table acts as a sort “forensic” roadmap of how the gas shale industry tries to tailor the frac chemistry to optimize the gas recovery from the Marcellus shale play in Pennsylvania

For example, hydrochloric acid (HCl, listed first) is used to “clean up” the area around wellbore from damage induced by drilling or the explosives used to initiate fracture propagation. HCl is commonly in all shale plays but is not necessarily related to its use in carbonate systems of conventional reservoirs. Water and proppant volumes can be diagnostic of the size of the synthetic permeability being created around the length of the wellbore.

Table 2. Compilation of the most commonly used additives in Pennsylvania Marcellus Shale Play (compiled from FracFocus.org).

Chemical name	CAS #	# of disclosures	Avg. max concentration by mass in fluid	Avg. of max concentration by mass in additive
Hydrochloric acid	7647-01-0	2,279	0.065%	15%
Methanol	67-56-1	1,633	0.00061%	40%
Distillates, petroleum, hydrotreated light	64742-47-8	1,434	0.021%	30%
Propargyl alcohol	107-19-7	1,371	0.000050%	10%
Glutaraldehyde	111-30-8	819	0.0040%	30%
Ethylene glycol	107-21-1	807	0.0047%	30%
2,2-Dibromo-3-nitrilopropionamide	10222-01-2	804	0.0050%	20%
Isopropanol	67-63-0	735	0.00029%	15%
Ammonium chloride	12125-02-9	732	0.0022%	10%
Citric acid	77-92-9	701	0.0012%	55%
Polyethylene glycol	25322-68-3	688	0.014%	60%
Guar gum	9000-30-0	538	0.0019%	100%
2-Butoxyethanol	111-76-2	498	0.00011%	15%
Sodium hydroxide	1310-73-2	406	0.0012%	1.0%
Ethanol	64-17-5	388	0.0013%	5.0%
Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides	68424-85-1	373	0.0023%	7.0%
Sodium persulfate	7775-27-1	373	0.000090%	100%
Hemicellulase enzyme	9012-54-8	367	0.000010%	15%
Tri-n-butyl tetradecyl phosphonium chloride	81741-28-8	350	0.0021%	10%
3,4,4-Trimethyloxazolidine	75673-43-7	299	0.00090%	5.0%
4,4-Dimethyloxazolidine	51200-87-4	299	0.014%	78%
Didecyl dimethyl ammonium chloride	7173-51-5	296	0.0023%	8.0%
Thiourea polymer	68527-49-1	280	0.00017%	30%
Sodium chloride	7647-14-5	275	0.0050%	7.5%

Crosslinkers and crosslinked-associated additives (Gelling agents) are highlighted in green, and consist of polymers and gels that are indicative of the levels of pressurization imposed on a frac fluid. The first important additive of interest is the distillates (64742-47-8) because they serve as a carrier fluid for borate or zirconate crosslinkers, which are used for elevated reservoir temperatures; the Marcellus is known to have higher than average Bottom Hole Temperatures (BHT > 60-70^{o}C). Distillates can also be used as a carrier fluid for polyacrylamide friction reducer (slickwater); slickwater being the most common treatment fluid used in all reservoir types in modern stimulation methods (Economides and Nolte, 2009). Guar gum (9000-30-0) is a gelling agent, which thickens the water in order to suspend the proppant for deeper delivery into the zone of enhanced fracture permeability. Gels are used frequently in the Marcellus because of the abnormally Bottom Hole Pressures (BHP > 5000 psi; refer to Fig. 2), and the increased viscosity of the fluid allows for better performance of deep proppant delivery. Sodium persulfate (7775-27-1) is then used to delay the breakdown of slicking polymers and gelling agents to allow for easier flowback once fluid flow is normalized during the beginning stages of production. In a similar capacity, hemicellulase enzymes (9012-54-8) are used to further break down guar gum-based gels. These "breakers" also reduce unwanted additives after stimulation, commonly referred to as residual waste (Economides and Nolte, 2009). Breakers are commonly used in the Marcellus because they are required anytime a gel or crosslinker is deployed in treatment. Other breakers include ethylene and polyethylene glycol.

Stabilizers and surfactants highlighted are in blue. Surfactants are used in multiphase reservoirs to lower the surface tension or interfacial tension between fluids or between a fluid and a solid - i.e., artificially enhance the effective pore throat diameter in a water-wet formation, Although the Marcellus is known primarily for dry gas production (methane only) it is common to have multiple varieties of hydrocarbon condensates with varying densities associated with the dry gas. Ethanol (64-17-5) is another stabilizing agent commonly used in conjunction with other surfactants. Didecyl dimethyl ammonium chloride (7173-51-5) is used as a clay stabilizer, which prevents clays from swelling or shifting. Again the purpose here is to enhance effective pore throat diameters thereby improving recovery efficiency. 2-Butoxyethanol (111-76-2) is another stabilizer (Economides and Nolte, 2009). Unsupported clays in the Marcellus are known to swell in water-based frac fluids that can then lead to reduced permeability within multiphase reservoirs. Sodium chloride (7647-14-5) is used for clay stabilization purpose as well.

Other common additives not necessarily related to the Marcellus geology in particular are the biocides, highlighted in yellow, and corrosion inhibitors highlighted in orange. Biocides (also known as disinfectants) are used to control the growth of certain kinds of microbes that would destroy gelled fracture fluids or generate a hydrogen sulfide (H_2S) gas souring problem in the reservoir (bacterial sulfate reduction or BSR). Over time the H_2S gas evolution can cause serious casing degradation leading to possible failure. The intent is for the biocides to eliminate bacteria in the reservoir that produce corrosive by-products. In this manner, the corrosion inhibitors bond to the metal surfaces of the downhole casing. This armoring process protects against the initial and subsequent acid treatments within a wellbore that could degrade subsurface metal through pit or crack formation, or development of oxidized iron. PH buffers are added in all frac fluid treatments, in this case sodium hydroxide (NaOH), highlighted in red. Maintaining a neutral pH is crucial to the integrity of additives, especially the gelling and crosslinking types. In this case the hydroxide helps balance the additives with a more acidic pH signature.

The known characteristics of the Marcellus shales match with the prototypical frac fluid of the region examined (Table 2). We see a chemical constituency that has been formulated for a formation with high pressure (refer to Figure 2), modest to high temperature (60-70^{o}C), low permeability, various pore geometries hosted by organic matter and moderate to high TOC.

DISCUSSION

Frac fluid disclosure records for a given formation can act somewhat like that of a LWD/MWD (logging while drilling/measurements-while-drilling) records – i.e., "forensic" road mapping indicators of the key hydraulic fracturing attributes of the formation. As wellbore engineering technology, frac fluid chemistry and stimulation methods advance, we observe the composition of a frac fluid change to match. Energy producers are constantly trying to meet domestic and foreign energy demands while realizing a profit. As conventional hydrocarbon recovery begins to reach its market cap potential, market demand will continue to grow. This "energy demand gap" will be filled by unconventional hydrocarbon development - e.g., tight gas, gas shales, oil sands or even underground coal gasification. North American Devonian shales are known to host significant hydrocarbon reserves that may last for many years, but only until recently has technology allowed for exploitation of those reserves. The Marcellus is an example of this kind of shale.

Through a data analytic assessment of the FracFocus data base, we compiled a hypothetical frac fluid additives list based on 2,279 fracturing treatment disclosures from 2011 to 2013 specifically for the Marcellus gas shale restricted to the state of Pennsylvania. The aggregated fluid data serves as a reference point, or norm for the Marcellus shale play in this region. This frac fluid encompasses all the major components we should expect to find that are compatible (specifically tailored) with the various subsurface characteristics of the Marcellus – e.g., moderate to high pressure and temperature with porosity hosted in submicron pores localized in the mature organic matter. The compounds selected to best match the Marcellus attributes are paired with the more common biocides and corrosion inhibitors used for decades in both conventional as well more recent unconventional systems. The chemical additive disclosure records provided by the FracFocus.org web site provide a “window” into the strategies used by industry to enhance hydrocarbon recovery from any formation in any basin where production is realized.

RECOMENDATIONS

The ability to access data bases identifying the frac chemicals of choice and their frequency offers opportunities to assess, at least in qualitative terms, some of the physical and chemical properties of the formation of interest. Horizontal and directional well bores (vertical included) can extend for several miles in the subsurface so the design of the frac treatment and associated chemical additives is a non-trivial challenge industry deals with regularly. Reservoirs are typically heterogeneous throughout and in fact can change markedly in a matter of a few 10's feet or less. To gain greater insight into the heterogeneous geology of the formation, we need detailed data obtained from smaller spatial increments. If a treatment zone of a wellbore is a total of 2,000 ft., for example, there may be 200 hundred individual stages that may be treated differently based on intrinsic characteristics of the formation (e.g., pressure, temperature, mineralogy, pore connectivity that controls local permeability, etc.). Data are needed on how the stages were actually treated versus how the schedule was originally devised.

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